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(71)Applicant : HITACHI METALS LTD
(72)Inventor : KATSURAGI SUSUMU
ONO TAKEHIRO

(54) LOW THERMAL EXPANSION Fe-BASE HEAT RESISTANT ALLOY, EXCELLENT IN HIGH TEMPERATURE STRENGTH

(57)Abstract:

PROBLEM TO BE SOLVED: To increase the high temperature strength of a low thermal expansion Fe-base heat resistant alloy.

SOLUTION: The alloy has a composition consisting of, by mass, ≤0.2% C, ≤1.0% Si, ≤2.0% Mn, 2.0-8.0% Cr, 1.0-2.0% Al, 1.2-2.5% Ti, 3.0-6.0% Nb, 30-35% Ni, 20-30% Co and the balance essentially Fe besides impurities and having the following relations: A value represented by (A value)=(Al+Ti+Nb), by mass, is ≥6.2%; B value represented by (B value) =3.44Al/(3.44Al+1.94Ti+ Nb), by mass% ratio, is 0.3-0.5; C value represented by (C value)=(Al/Ti), by atomic % ratio, is 1.1-1.8; and D value represented by (D value)=(Ti/Nb), by atomic % ratio, is 0.4-1.0. Moreover this alloy has the following: ≥500 MPa high temperature tensile strength at 800°C; ≤12 ×10-6/°C average coefficient of thermal expansion at 30-500°C; and ≤ 3.0g/m2 increase in quantity of oxide after heating for 100 h in the air of 800°C.

all but claim5

C
Si
Mn
P
Ni
Cr
S
N

CLAIMS

[Claim(s)]

[Claim 1] In mass %, C:0.2 or less, less than [Si:1.0], less than [Mn:2.0], Cr:2.0-8.0, aluminum:1.0-2.0, Ti:1.2-2.5, Nb:3.0-6.0, nickel:30-35, and Co:20-30 are contained. By and mass % By more than A Value =(aluminum+Ti+Nb):6.2 and the mass % ratio, by B value =3.44aluminum/(3.44aluminum+1.94 Ti+Nb):0.3-0.5 and atomic % ratio C-value =(aluminum/Ti): It is the high intensity Fe radical heat-resistant alloy of the low thermal expansion which has the relation of 1.1-1.8 and D value =(Ti/Nb):0.4-1.0, and was excellent in the oxidation resistance characterized by the remainder consisting of Fe substantially except for an impurity.

[Claim 2] Furthermore, the high intensity Fe radical heat-resistant alloy of a low thermal expansion excellent in the oxidation resistance according to claim 1 characterized by containing one sort of Mo and W not more than :(Mo+0.5W) 3.0, or two sorts in mass %.

[Claim 3] As the 1st group, in mass % furthermore, as one sort B:0.02 or less and not more than Zr:0.1 or two sorts, and the 2nd group In mass %, as one sort Y:0.2 or less and not more than REM:0.2 or two sorts, and the 3rd group The high intensity Fe radical heat-resistant alloy of a low thermal expansion excellent in the oxidation resistance according to claim 1 or 2 characterized by including one group of one sort less than [Mg0.02%] and not more than calcium0.02% or two sorts, and ********, or two or more groups in mass %.

[Claim 4] For a 30-500-degree C average coefficient of thermal expansion, at 500 or more MPas, the oxidation loading after 100hr heating is [the elevated-temperature tensile strength in 800 degrees C] 3.0 g/m2 in 800-degree C atmospheric air less than [12x10-6/degree C]. High intensity Fe radical heat-resistant alloy of a low thermal expansion excellent in oxidation resistance given in either of claims 1-3 characterized by being the following.

[Translation done.]

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Industrial Application] This invention relates to the heat-resistant alloy for which it excels in the reinforcement of ordinary temperature, the oxidation resistance in an elevated temperature, and reinforcement, and a low coefficient of thermal expansion is needed. It is related with the high intensity heat-resistant alloy of the low thermal expansion used for the composite components especially used for the ceramics or cemented carbide, joining, a gas turbine member, etc.
[0002]
[Description of the Prior Art] In recent years, the alloy equipped with higher proof stress and tensile strength from the ordinary temperature to the elevated temperature is required with lifting of the service temperature of gas turbine components. Simultaneous, like the turbo color which joins the ceramic rotor and metal shaft of a turbocharger, in order to maintain various kinds of components and the path clearance between members to a constant rate from ordinary temperature to an elevated temperature as a metallic material used for low thermal expansion ingredients, such as ceramics and cemented carbide, joining, the ingredient with a low coefficient of thermal expansion is demanded.
[0003] That is, though it is low thermal expansion as such an application, the demand of the metallic material which has high temperature strength is increasing increasingly. Furthermore, the oxidation-resistant improvement at the time of using it for these applications at an elevated temperature is demanded.
[0004] As an alloy applicable to this application A low thermal expansion alloy given in JP,53-6225,A (They are nickel:30-57, Cr:1.7-8.3, Ti:1-2, Nb+0.5Ta:1.5-5.0, Co:<=31, aluminum<=1.5, C:<=0.2, Mn:<=2.0.Si:<=1.0, B:<=0.03, and Remainder Fe at mass %) The alloy which the invention-in-this-application person etc. indicated in JP,6-228714,A previously (C:0.2 or less by mass %) Si: Less than [1.0], less than [Mn:2.0], and Cr:4 are exceeded, 10 or less and aluminum:1.0 are exceeded, and there are less than [more than nickel:20 30], Co:20-35, etc. by 2.0 or less, Ti:0.3-3.0, Nb+0.5, and Ta:1.5-7.
[0005] Moreover, in nickel radical heat-resistant alloy with good high temperature strength, WASPALOY (trademark of United Technologies) is typical. This alloy is used for the components of the jet engine with which severe high temperature strength and severe oxidation resistance are demanded etc.
[0006]
[Problem(s) to be Solved by the Invention] If plastic deformation is easily caused at an elevated temperature in the case of the metallic material used as joint material with low thermal expansion ingredients, such as ceramics, the function as joint material cannot be achieved. Therefore, this application requires high proof stress together with hot high tensile strength with a low coefficient of thermal expansion. Moreover, it must take into consideration that an ingredient with which an embrittlement phase will deposit and reinforcement will fall if it is simultaneously used at an elevated temperature for a long time cannot be used at an elevated temperature.
[0007] However, it is admitted that an organization destabilizes and high temperature strength falls when the low thermal expansion alloy indicated by said JP,53-6225,A is put to the elevated temperature to about 900 degrees C for a long time exceeding 700 degrees C. Moreover, since there are also few contents of Co to a rate with nickel, lowering raising and high temperature strength is admitted in a coefficient of thermal expansion. About high temperature strength, it is understood as originating in that there are few total amounts of Ti and Nb which form gamma'phase other than aluminum. Moreover, since nickel is less than 30% similarly, when the elevated-temperature long duration activity also of the alloy indicated by JP,6-228714,A which the invention-in-this-application person etc. indicated is carried out, a base organization may destabilize and high temperature strength may fall. Therefore, it cannot be said that the above-mentioned existing alloy is fully satisfied as a metallic material used for the above-mentioned application.
[0008] Moreover, although it shows good high temperature strength and the outstanding oxidation

resistance, since nickel radical heat-resistant alloy represented by said WASPALOY is austenite, its coefficient of thermal expansion is high, and is unsuitable for using it for the above-mentioned application.

[0009] Then, having the same low coefficient of thermal expansion as the existing alloy given [above-mentioned] in JP,53-6225,A, rather than this alloy, hot structural stability is good and this invention aims to let it to excel in oxidation resistance and offer the high intensity Fe radical heat-resistant alloy of low thermal expansion with reinforcement high from the ordinary temperature near nickel radical heat-resistant alloy to an elevated temperature. It is in offering the heat-resistant alloy which fitted components, such as a gas turbine member, and ceramics, composite with cemented carbide, especially.

[0010]

[Means for Solving the Problem] Invention-in-this-application persons resulted in this invention that it was important to stabilize more gamma' (gamma prime) phase which is gamma (austenite) phase and the precipitation-strengthening phase which are a base by introducing the concept of a header, Following A, B and C, and a D value, in order to raise high temperature strength further that the above-mentioned trouble should be solved, as a result of experimenting for a Fe-Co-nickel system alloy.

[0011] Namely, the high intensity Fe radical heat-resistant alloy of a low thermal expansion excellent in the oxidation resistance of this invention In mass %, C:0.2 or less, less than [Si:1.0], less than [Mn:2.0], Cr:2.0-8.0, aluminum:1.0-2.0, Ti:1.2-2.5, Nb:3.0-6.0, nickel:30-35, and Co:20-30 are contained. By and mass % By more than A Value =(aluminum+Ti+Nb):6.2 and the mass % ratio, by B value =3.44aluminum/(3.44aluminum+1.94 Ti+Nb):0.3-0.5 and atomic % ratio C-value = (aluminum/Ti): It has the relation of 1.1-1.8 and D value =(Ti/Nb):0.4-1.0, and is characterized by the remainder consisting of Fe substantially except for an impurity.

[0012] Moreover, the high intensity Fe radical heat-resistant alloy of a low thermal expansion excellent in the oxidation resistance of this invention Things are made. containing one sort of Mo and W not more than :(Mo+0.5W) 3.0, or two sorts in mass % -- as the 1st group further In mass %, as one sort B:0.02 or less and not more than Zr:0.1 or two sorts, and the 2nd group In mass %, one group of one sort less than [Mg0.02%] and not more than calcium0.02% or two sorts, and ******** or two or more groups can be included by mass % as one sort Y:0.2 or less and not more than REM:0.2 or two sorts, and the 3rd group.

[0013] Moreover, elevated-temperature tensile strength [in / in the high intensity Fe radical heat-resistant alloy of a low thermal expansion excellent in the oxidation resistance of this invention / 800 degrees C] is 500 or more MPas, a 30-500-degree C average coefficient of thermal expansion is less than [12x10-6/degree C], and the oxidation loading after 100hr heating is 3.0 g/m2 in 800-degree C atmospheric air. It is characterized by being the following.

[0014] gamma' phase which is the above-mentioned precipitation-strengthening phase is the intermetallic compound which consists of nickel3 aluminum, and after various consolidation elements other than aluminum, such as Ti, Nb, Cr, and Mo, have dissolved, it exists. Especially the elements dissolved and strengthened to the aluminum side in gamma' phase are Ti and Nb. The heat-resistant alloy of this invention attained stabilization of gamma' phase by introducing A, above-mentioned B and above-mentioned C, and the concept of a D value, and controlling the addition of three elements of aluminum, Ti, and Nb.

[0015] That is, higher high temperature strength was able to be obtained by making A value of the total amount of addition 3 elements aluminum, Ti, and Nb or more into 6.2 by mass %. Moreover, when a mass % ratio describes B value of the quantitative ratio of aluminum occupied in addition 3 element on the basis of Nb, it is expressed with B value =3.44aluminum/(3.44aluminum+1.94 Ti+Nb). B value of this aluminum quantitative ratio was made into within the limits of 0.3-0.5, and related C value =aluminum/Ti of aluminum and Ti was set to 1.2-1.8 by atomic % ratio, and it was conventionally made clearer than an alloy by controlling related D value =Ti/Nb of Ti and Nb to be set to 0.4-1.0 by atomic % ratio that the organization which was made to stabilize gamma' phase and was stabilized more to the pyrosphere, and a good mechanical property were acquired.

[0016] As mentioned above, in order to raise high temperature strength, it is an effective means to make

the amount of the element which constitutes gamma' phase increase, and this invention alloy was able to obtain high aluminum quantitative ratio in gamma' phase by making the amount of aluminum into the addition exceeding 1.0% higher than the conventional low thermal expansion heat-resistant alloy. Hot-working nature and high temperature strength were able to be reconciled by finding out large Ti of effectiveness and the optimal addition range of Nb which are that over there and carry out solid solution strengthening of the gamma' phase other than aluminum in the direction which leads to on the other hand the amount of deposits of the high amount of aluminum of gamma' phase increasing, and injures hot-working nature.

[0017] When the addition of Ti was increased and long duration maintenance is carried out at the elevated temperature to 900 degrees C exceeding 700 degrees C, since gamma' phase metamorphoses into eta phase which does not contribute to a consolidation, high temperature strength falls. Then, this invention alloy was able to control the transformation to eta phase by controlling the C value of an aluminum/Ti ratio. Moreover, it considered acquiring a good mechanical property by controlling the D value of a Ti/Nb ratio in a certain range by controlling the D value of (Hitachi Metals technical report No.3 (1986)) and a Ti/Nb ratio from the knowledge of high elevated-temperature proof stress being acquired.

[0018] Moreover, this invention alloy aims at raising oxidation resistance. Although Cr is effective in raising oxidation resistance, a coefficient of thermal expansion is enlarged. Then, this invention alloy was able to aim at coexistence of a low thermal expansion property and elevated-temperature oxidation resistance by finding out large nickel of the effectiveness of lowering a coefficient of thermal expansion, Co, and the optimal addition range of Cr.

[0019] this invention person etc. was able to find out the high intensity heat-resistant alloy of a low thermal expansion excellent in the oxidation resistance which has the stable organization and a good mechanical property by controlling the amount and quantitative ratio of an element which constitute gamma' phase from the above examination result.

[0020]

[Embodiment of the Invention] Hereafter, the reason for component definition of this invention alloy is explained. Although C combines with Ti or Nb, and forms carbide, big and rough-ization of crystal grain is prevented and it contributes to improvement in reinforcement, since too much addition exceeding 0.2% decreases Ti and Nb of a base which act considering the carbide of Ti or Nb as increase and a precipitation-strengthening element and increases the coefficient of thermal expansion of an alloy, C may be 0.2% or less. The range of desirable C is 0.1% or less.

[0021] Since Si promotes the deposit of the Laves phase which improves grain refining and the grain boundary configuration other than the effectiveness as a deoxidizer, and raises the reinforcement of a grain boundary, it is an indispensable alloying element. A Laves phase considers Fe2 (Nb, Ta) as a basic presentation, and Si dissolves to the Nb side and promotes a deposit. When an operation of this crystal stressing carries out little addition of the Si, effectiveness shows up. However, since too much addition exceeding 1.0% causes lowering of hot-working nature and high temperature strength, Si is limited to 1.0% or less. The range of more desirable Si is 0.2 - 0.6% of range.

[0022] Since Mn is added as a deoxidizer, it is contained in an alloy, but since too much addition makes the coefficient of thermal expansion of an alloy increase, it is not desirable. Therefore, Mn is limited to 2.0% or less. It is 1.0% or less more desirably.

[0023] Cr is Cr 2O3 at the time of heating at high temperature. An oxide film is formed and there is work which oxidation resistance is improved [work] and raises high temperature strength. Therefore, although Cr needs addition exceeding at least 2.0%, too much addition exceeding 8.0% lowers the Curie point to reverse, and makes a coefficient of thermal expansion increase. For this reason, however it may adjust Fe which constitutes a matrix, and the ratio of Co and nickel, sufficient low thermal expansion property will no longer be acquired. Therefore, Cr is limited to 2.0% - 8.0% of range. The more desirable range of Cr of the desirable range of Cr is 2.5 - 4.5% 2.2 to 6.0%.

[0024] aluminum is an element which constitutes gamma' phase which is the precipitation-strengthening mold particle which raises ordinary temperature and high temperature strength in this invention alloy,

and is the most important element in this invention. By aging treatment, aluminum deposits detailed gamma' phase of about 10nm of the diameter number of the presentations which consist of 3 (nickel, Co) (aluminum, Ti, Nb), and raises remarkably elevated-temperature tensile strength and the creep rupture strength of elevated-temperature long duration. If the concentration of aluminum in gamma' phase falls, gamma' phase will become unstable at an about 700-900-degree C elevated temperature, hexagonal eta (ITA) phase and delta (delta) phase of a prismatic crystal will deposit, and high temperature strength will fall remarkably. Therefore, in order to obtain high aluminum quantitative ratio in the inside of gamma' phase, aluminum needs addition exceeding at least 1.0%.

[0025] However, even if the concentration of aluminum in gamma' phase increases too much, the gamma' phase itself is not fully strengthened and high temperature strength does not become high enough. Moreover, since too much addition exceeding 2.0% deposits gamma' phase so much and hot-working nature is reduced, aluminum is limited to 1.0 - 2.0%.

[0026] Ti and Nb combine with C first, they form carbide, they combine with nickel, Co, etc. with aluminum so that remaining Ti and remaining Nb may explain below, they form gamma' phase, and strengthen an alloy. By aging treatment, Ti deposits gamma' phase with nickel, Co, aluminum, and Nb, and raises elevated-temperature tensile strength remarkably. Therefore, although the required amount of Ti is at least 1.2%, since too much addition exceeding 2.5% causes the increment in a coefficient of thermal expansion, and lowering of hot-working nature while making gamma' phase instability, Ti is limited to 1.2 - 2.5%. The more desirable addition range is 1.2 - 2.0%.

[0027] Like Ti, by aging treatment, Nb deposits gamma' phase with nickel, Co, and aluminum, and raises **** reinforcement remarkably. A part of [further] Nb(s) have the operation which raises the reinforcement of a grain boundary, and have the operation which raises remarkably whenever [elevated-temperature tensile strength and creep-rupture-strength] while they deposit a Laves phase with a diameter of about several micrometers in a grain boundary and a grain and make crystal grain detailed. Therefore, Nb is taken as 3.0 - 6.0% of addition. The more desirable addition range is 3.5 - 4.5%.

[0028] If it sees about the total amount of aluminum, Ti, and Nb which constitute gamma' phase and this will be increased, high temperature strength can be raised remarkably, and if the total amount of aluminum, Ti, and Nb exceeds 6.2%, higher high temperature strength will be obtained by depositing a lot of intermetallic compounds (delta phase, gamma' phase) at the time of aging treatment. Then, A value = (aluminum+Ti+Nb) of the total amount of aluminum, Ti, and Nb could be 6.2% or more.

[0029] Moreover, aluminum needs to control strictly the rate of aluminum occupied to the addition of three elements of aluminum, Ti, and Nb which constitute the aluminum side out of [other than the component convention by the above aluminum independent] gamma' phase in order to deposit stable gamma' phase.

[0030] When the quantitative ratio of aluminum occupied in addition 3 element is based on Nb, it is a mass % ratio and is expressed with B value =3.44aluminum/(3.44aluminum+1.94 Ti+Nb). If B value of this aluminum quantitative ratio is smaller than 0.3, reinforcement sufficient because gamma' phase becomes instability will no longer be obtained in the state of elevated-temperature long duration heating. On the other hand, if B value of this aluminum quantitative ratio exceeds 0.5, gamma' phase will become stability, but since a consolidation is not fully carried out, high temperature strength falls on the contrary. Therefore, in order to stabilize gamma' phase to a pyrosphere and to obtain reinforcement conventionally higher than an alloy, it is required for B value =3.44aluminum/(3.44aluminum+1.94 Ti+Nb) to be within the limits of 0.3-0.5. More suitable range is 0.35-0.45.

[0031] The C value of an aluminum/Ti ratio (atomic % ratio) is important when gamma' phase is constituted. Since gamma' phase will metamorphose into eta phase which is a stability phase which does not contribute to a consolidation when long duration maintenance is carried out at an elevated temperature 700 degrees C or more if the C value of an aluminum/Ti ratio is smaller than 1.1, there is a danger that high temperature strength will fall greatly. Moreover, if 1.8 is exceeded, gamma' phase will become stability, but since a consolidation is not fully carried out, reinforcement cannot fully be raised but high temperature strength comes to fall on the contrary. Therefore, C value of an aluminum/Ti ratio was set to 1.1-1.8. More suitable range is 1.3-1.7.

[0032] Moreover, it is important when the D value of a Ti/Nb ratio (atomic % ratio) also constitutes gamma' phase. If the D value of a Ti/Nb ratio is smaller than 0.4, the rate of Nb which dissolves to gamma' phase will increase, and proof stress will go up, but since cold-working nature and hot-working nature fall greatly, it is not desirable. Moreover, it is not desirable when it becomes easy to deform an ingredient plastically when carrying out a long duration activity at an elevated temperature, in order that proof stress may decline greatly, if the D value of a Ti/Nb ratio exceeds 1.0, and junction nature with the ceramics is called for in an elevated temperature. Therefore, the D value of a Ti/Nb ratio was set to 0.4-1.0. More desirable range is 0.6-0.8.
[0033] nickel constitutes a matrix with Co and Fe and Fe and the ratio of Co and nickel affect remarkably the deposit gestalt of the coefficient of thermal expansion of an alloy, and an intermetallic compound. Although this invention alloy contains many precipitation-strengthening elements, such as Ti, Nb, and aluminum, in order to give the high temperature strength of the highest level conventionally exceeding an alloy, it finds out the rate of Fe, Co, and nickel which are not in an alloy conventionally simultaneously, and enables coexistence of high elevated-temperature tensile strength and a low coefficient of thermal expansion. That is, the amount of deposits of a detailed spherical Laves phase increases, it is useful to crystal stressing with Fe of this invention alloy, amount, and rate of Co and nickel, and hot creep-rupture-strength reinforcement is raised.
[0034] Since nickel is also the configuration element of gamma' phase, also after gamma' phase fully deposits and deposits, sufficient amount of nickel from which a base can serve as a stable austenite phase is required for it. Therefore, the required amount of nickel is 30% or more. Since 35% or more of nickel makes a coefficient of thermal expansion increase and decreases the amount of deposits of a Laves phase, detailed-izing and crystal stressing of crystal grain become difficult, and it becomes impossible conversely, to attain the object of this invention. Therefore, it is important for nickel that it is 30 - 35%. The range of desirable nickel is 30.5 - 32.5%.
[0035] Co as well as nickel constitutes a matrix with Fe, and is useful to lowering of a coefficient of thermal expansion, and the deposit of a Laves phase. A part of [further] Co(es) dissolve to the nickel side in gamma' phase. Therefore, Co needs 20% or more of addition. Conversely, addition of Co exceeding 30% imitates the increment in a coefficient of thermal expansion, and lowering of the high temperature strength accompanying too much Laves phase deposit, it is that of ** and Co is taken as 20 - 30% of range. The desirable range of Co is 22 - 28%.
[0036] Although Mo and W are not indispensable alloying elements in this invention alloy, they can strengthen a matrix with adding one sort in both, or two sorts, and can raise hot reinforcement more by it. However, since both both raise the coefficient of thermal expansion of an alloy, too much addition is not desirable. Both are congeneric elements and Mo of W is advantageous in oxidation resistance from the field of specific gravity. When adding Mo and W in this invention, it considers as 3.0% or less of addition by (Mo+0.5W). If it is this amount, high temperature strength will improve without injuring the thermal expansion property of this invention alloy, oxidation resistance, and especially specific gravity.
[0037] B and Zr are one sort or two sorts of addition, they are segregated to the grain boundary, raise grain boundary reinforcement, and contribute to improvement in hot-working nature and creep rupture strength. Since the effectiveness shows up from addition of a **** minute amount, a lot of addition reduces the initial melting temperature of an alloy conversely and hot-working nature is injured, in B, it limits to 0.02% or less, and, in the case of Zr, limits to 0.1% or less.
[0038] Moreover, one sort of Y and a rare earth metal (REM) or two sorts are Cr 2O3 by respectively independent and compound. Since adhesion is increased and it contributes to an oxidation-resistant improvement, it can add as a selection element. Although the effectiveness of an oxidation-resistant improvement of Y and REM shows up from both very little addition, since Y or REM, and the intermetallic compound of nickel, Fe, and Co are crystallized and the eutectic temperature becomes lower than the hot-working temperature of an alloy, too much addition reduces the hot-working nature of an alloy. Therefore, Y takes and REM is taken as 0.2% or less of addition 0.2% or less.
[0039] Furthermore, as a selection alloying element, adding one sort of Mg and calcium or two sorts has respectively independent and the effectiveness which raises the hot-working nature of an alloy, and

elevated-temperature ductility while heightening the deoxidation / desulfurization effectiveness by compound. Therefore, Mg can be added and calcium can be added in 0.02% or less of range 0.02% or less.
[0040] Although it will not become especially a problem on a property if the following alloy element is contained in the range shown below besides an above-mentioned addition alloy element, the one as much as possible where all are lower is desirable. Everything but O<=0.005 and the element described N<=0.005% or more is constituted from mass % by Remainder Fe V<=1%, Cu<=1%, Re<=1%, Hf<=0.2%, P<=0.01%, and S<=0.005%.
[0041] Next, the reason for having specified the property of this invention alloy is explained. Since an ingredient will become soft in case it is an activity if high temperature strength is low, it stops achieving the function as joint material. As reinforcement demanded in order to achieve this function, the elevated-temperature tensile strength in 800 degrees C specified 500 or more MPas.
[0042] Moreover, if a hot coefficient of thermal expansion becomes large, since it will become difficult to keep constant the path clearance between each part article or a member from ordinary temperature to an elevated temperature, a low coefficient of thermal expansion with the alloy near the ceramics etc. is required. Then, the 30-500-degree C average coefficient of thermal expansion was specified less than [12x10-6/degree C].
[0043] Furthermore, if the alloy which is not oxidation-resistant fitness is used in an elevated temperature, the adhesion of the oxidizing zone to form is inadequate, and since an oxidizing zone exfoliates, it will become difficult for junction between each part article or a member to deteriorate, and to keep path clearance constant from ordinary temperature to an elevated temperature. Then, it is oxidation loading after 100hr heating in 800-degree C atmospheric air as a numeric value which is precise, forms the good oxidizing zone of adhesion, and shows good oxidation resistance 3.0 g/m2 It considered as the following.
[0044] As for the ingot of this invention alloy, being manufactured by vacuum melting is desirable. ingot
When ingot weight is 200-300kg or less, a property only with the vacuous good 1-time dissolution is acquired, but when manufacturing the ingot of bigger weight than it, manufacture of the ingot by high remelting of organization improvement effects, such as electroslag remelting and vacuum arc remelting, is more desirable.
[0045] Hot forming is possible for such an ingot by the same hot-working process as usual superalloy. Furthermore, shaping between the colds can be added if needed, and the target product configuration can be made. A solution treatment is performed in the temperature requirement where gamma' phase fully dissolves while a Laves phase remains or deposits. The desirable temperature of a solution treatment is 850-1100 degrees C. When hot working before a solution treatment can substitute for a solution treatment, it may omit a solution treatment. Aging treatment is carried out at the temperature which gamma' phase has consistency enough with a base, and deposits as about several 10nm detailed deposit particle. The desirable temperature requirement of aging treatment is 600-850 degrees C.
[0046]
[Example] It dissolved with the vacuum induction melting furnace, and the alloy of the chemical composition shown in a table 1 and a table 2 was made into the 10kg ingot. No.1-9 are this invention alloy and No.11 are the conventional alloy given in said JP,6-228714,A. No. of a comparison alloy -- the Cr additive-free alloy with which 21 and 22 are similar to an alloy given in said JP,53-6225,A, and No.23 are similar to No.22, and No.24 are the alloys of the component equivalent to WASPALOY of nickel **-SU. Moreover, it combines with a table 2 and the calculated value of said A, B and C, and a D value is shown.
[0047]
[A table 1]

		C	Si	Mn	Ni	Cr	W	Mo	Co	Al	Ti	Nb	B
本発明合金	No.1	0.035	0.45	0.21	31.5	6.2			23.8	1.08	1.18	4.43	0.005
	No.2	0.035	0.42	0.10	31.5	5.9			23.8	1.19	1.35	4.07	0.004
	No.3	0.038	0.50	0.18	30.1	3.9			23.8	1.18	1.29	3.82	0.004
	No.4	0.034	0.35	0.15	31.3	4.1			24.0	1.42	1.51	3.62	0.006
	No.5	0.039	0.48	0.22	31.7	5.0			26.3	1.21	1.31	4.51	0.004
	No.6	0.039	0.61	0.18	32.6	4.8			25.1	1.41	1.88	4.01	0.005
	No.7	0.034	0.45	0.15	34.2	7.2			25.4	1.28	1.51	3.91	0.004
	No.8	0.033	0.42	0.12	30.9	3.1			23.5	1.31	1.48	3.64	0.003
	No.9	0.041	0.41	0.31	31.2	4.2	0.8	1	22.5	1.29	1.39	3.91	0.005
従来合金	No.11	0.033	0.41	0.21	28.8	6.0			25.0	1.10	1.00	3.90	0.003
比較合金	No.21	0.021	0.09	0.18	33.9	2.0			19.7	0.82	1.49	1.88	0.004
	No.22	0.023	0.11	0.21	38.3	3.0			15.3	0.95	1.39	3.21	0.003
	No.23	0.035	0.42	0.19	28.2	0.0			19.5	0.60	1.38	4.20	0.005
	No.24	0.027	0.02	0.01	Bal.	14.5		4.3	13.4	1.47	3.12		0.005

[0048]
[A table 2]

	Zr	Y	REM	Mg	Ca	Fe	A値	B値	C値	D値
No.1			0.02	0.001		Bal.	6.69	0.36	1.69	0.52
No.2				0.001		Bal.	6.61	0.38	1.63	0.64
No.3				0.002		Bal.	6.29	0.39	1.70	0.66
No.4				0.001	0.002	Bal.	6.55	0.43	1.74	0.81
No.5		0.01		0.003		Bal.	7.03	0.37	1.71	0.56
No.6	0.03			0.001		Bal.	7.30	0.39	1.39	0.91
No.7				0.001		Bal.	6.70	0.39	1.56	0.75
No.8				0.002	0.003	Bal.	6.43	0.41	1.63	0.79
No.9				0.002		Bal.	6.59	0.40	1.73	0.69
No.11				0.001		Bal.	6.00	0.39	2.04	0.50
No.21				0.003		Bal.	4.19	0.37	1.04	1.50
No.22				0.002		Bal.	5.55	0.36	1.24	0.85
No.23				0.002		Bal.	6.18	0.23	0.80	0.64
No.24				0.002		0.5	4.59	0.46	0.87	-

A値: [Al%]+[Ti%]+[Nb%]
B値: 3.44*[Al%]／(3.44*[Al%]+1.94*[Ti%]+[Nb%])
C値: [Al at%]／[Ti at%]
D値: [Ti at%]／[Nb at%]

[0049] Cogging of the ingot of each above-mentioned alloy was carried out between heat, and it was made into the sample of 30mm angle. Then, the solution treatment which carries out after [980 degree-Cx1hr maintenance] water cooling of all the alloys was performed. Aging treatment cooled the alloy of No.1-9, and 11, 21-23 to 620 degrees C with the cooling rate of 55 degrees C/hr after 720 degree-Cx8hr maintenance, and heat-treated air cooling after 8h maintenance succeedingly. After carrying out after [843 degree-Cx4hr maintenance] air cooling of the No.24 alloy, it performed two-step aging treatment which carries out after [760 more degree-Cx16hr maintenance] air cooling.
[0050] About each of this test piece, ordinary temperature and a hot tension test, thermodilatometry, and an elevated-temperature anti-oxidation trial were performed. The elevated temperature tensile test was carried out based on the test method of ASTM in 800 degrees C with the parallel part diameter of 6.35mm, and the test piece for tensile test of 25.4mm of gauge length, and measured tensile strength and 0.2% proof stress. Measurement of a coefficient of thermal expansion measured the average coefficient of thermal expansion to 30 degrees C to 500 degrees C, and 800 degrees C with differential thermodilatometer. After the anti-oxidation trial heated 800 degree-Cx100hr for the round bar test piece with a diameter [of 10mm], and a die length of 20mm in the ambient atmosphere in atmospheric air, it measured the oxidation loading value and evaluated oxidation resistance. A mechanical property is shown in a table 3.
[0051]
[A table 3]

		常温引張特性				高温(800℃)引張特性			
		耐力(MPa)	引張強さ(MPa)	耐力比	伸び(%)	耐力(MPa)	引張強さ(MPa)	耐力比	伸び(%)
本発明合金	No.1	1051	1425	0.74	20.3	532	623	0.85	47.1
	No.2	1109	1429	0.78	15.9	551	612	0.90	41.3
	No.3	1079	1399	0.77	15.1	445	502	0.89	58.2
	No.4	1085	1425	0.76	14.2	439	509	0.86	60.2
	No.5	1135	1462	0.78	12.9	572	652	0.88	32.5
	No.6	1062	1432	0.74	19.5	592	675	0.88	35.7
	No.7	1095	1418	0.77	15.2	524	605	0.87	45.2
	No.8	1042	1421	0.73	20.5	449	511	0.88	55.9
	No.9	1060	1413	0.75	19.8	465	535	0.87	54.8
従来合金	No.11	952	1279	0.74	25.1	352	409	0.86	134.8
比較合金	No.21	940	1261	0.75	17.4	147	195	0.75	172.1
	No.22	938	1265	0.74	20.8	180	248	0.73	164.2
	No.23	1067	1382	0.77	20.1	201	274	0.73	152.9
	No.24	935	1352	0.69	28.6	625	730	0.86	22.8

[0052] From a table 3, if the tractive characteristics of ordinary temperature are seen first, the tensile strength of alloy No.1-9 of this invention is 1400MPa bases, and has high reinforcement as compared with conventional alloy No.11 of a 1200 - 1300MPa base, or comparison alloy No.21-24. The same is said of proof stress.
[0053] Also in the elevated-temperature tensile strength of 800 degrees C, although this invention alloy is inferior to comparison alloy No.24 (WASPALOY) of typical nickel radical heat-resistant alloy, it has dramatically excellent tensile strength and a proof stress ratio (proof stress/tensile strength) in Fe radical heat-resistant alloy of low thermal expansion.
[0054] That is, if it sees with elevated-temperature tensile strength, each this invention alloy No.1-9 shows the tensile strength of 500 or more MPas, and it has good elevated-temperature tensile strength. Although this value is lower than comparison alloy No.24 (WASPALOY) of nickel radical, it is the reinforcement which was not obtained in the conventional low expansion alloy as a Fe radical alloy. Alloy No.6 with highest A value also in this have the highest elevated-temperature tensile strength. On the other hand, as for alloy No.2 with B value and C value higher even if A value is high, or No.7, reinforcement becomes a little low as compared with No.6. Moreover, No.2 with few amounts of Cr(s) also in an invention alloy, No.3, and No.8 show lower elevated-temperature tensile strength. The above-mentioned data show that Cr has effectiveness in improvement in elevated-temperature tensile strength. On the other hand, the elevated-temperature tensile strength of comparison alloy No.21-23 is about 200 to 270 MPa. Thus, this invention alloy shows good elevated-temperature tensile strength, because all the default value of A, B, C, and D other than a chemical entity is satisfied. conventional alloy No.11 -- everything but the amount of Ti -- A value -- in comparison alloy No.21, since No.23 have B value and low C value, as for No.22, elevated-temperature tensile strength is [A value and C value / A value] all low.
[0055] Hot 0.2% proof stress is also higher than conventional alloy No.11 and comparison alloy No.21-23, and even if it sees that of this invention alloy No.1-9 by the proof stress ratio (proof stress/tensile strength), it is farther [than No.21-23] high. this invention alloy has reinforcement high from ordinary temperature to an elevated temperature as mentioned above.
[0056] The data of a coefficient of expansion and oxidization loading are shown in a table 4.
[0057]
[A table 4]

		平均熱膨張係数(30℃～500℃)	平均熱膨張係数(30℃～800℃)	酸化増量(800℃×100hr)
		/℃(×10-6)	/℃(×10-6)	(mg/cm2)
本発明合金	No.1	11.2	14.8	0.16
	No.2	10.9	14.6	0.18
	No.3	10.5	14.8	0.15
	No.4	10.6	14.7	0.11
	No.5	11.1	14.9	0.08
	No.6	11.3	14.9	0.06
	No.7	11.4	15.0	0.05
	No.8	9.6	14.6	0.24
	No.9	9.4	14.8	0.17
従来合金	No.11	11.6	15.2	0.21
比較合金	No.21	12.2	15.6	0.25
	No.22	12.6	16.1	0.21
	No.23	7.3	12.4	21.4
	No.24	13.8	15.8	0.43

[0058] if a coefficient of thermal expansion is seen -- this invention alloy -- 30-500 degrees C -- setting -- 9.4 - 11.4x10-6/degree C and 30-800 degrees C -- setting -- about -- 14.8x10-6/degree C -- it is -- conventional alloy No.11 and comparison alloy No. -- a low thermal expansion almost equivalent to 21 and 22 is shown. This value is a value lower than No.24 of nickel radical. Moreover, since comparison alloy No.23 do not contain Cr, although a coefficient of thermal expansion is low, it is remarkably inferior in the following oxidation resistance.

[0059] If it sees about oxidation resistance, although the coefficient of thermal expansion of No.23 alloy which made Cr additive-free as mentioned above is low, since it is Cr additive-free, oxidation resistance will fall. this invention alloy has the oxidation resistance more than an EQC as compared with conventional alloy No.11 and comparison alloy No.21-23, and even if it compares with No.24 alloy (WASPALOY) which is the representation of the conventional nickel **-SU alloy, it has higher oxidation resistance.

[0060] this invention alloy is Fe radical heat-resistant alloy which has the reinforcement higher than these alloys from ordinary temperature to an elevated temperature as mentioned above, having a coefficient of thermal expansion equivalent to the conventional low thermal expansion heat-resistant alloy. Moreover, also in elevated-temperature oxidation resistance, an alloy and nickel radical heat-resistant alloy are excelled conventionally.

[0061]

[Effect of the Invention] If the alloy of this invention is used for the application of gas turbine components, a ceramic joint article, a cemented carbide joint article, etc. Can be simultaneously satisfied with an alloy of the high high temperature strength which was not obtained, high elevated-temperature oxidation resistance, and a low thermal expansion property conventionally. From ordinary temperature to an elevated temperature with high intensity And the adaptation of the long duration to a required structural material of maintaining the path clearance prepared between various kinds of members or components to a constant rate from ordinary temperature to an elevated temperature is attained. Moreover, on the occasion of junction into the ceramics or a low thermal expansion ingredient like cemented carbide, reliable junction can cover long duration with high intensity. Furthermore, if it is the components which employed efficiently the feature of the high temperature strength which an invention alloy has, oxidation resistance, and a thermal expansion property even if it faces application on components other than these applications, a property with good all will be acquired.

[Translation done.]

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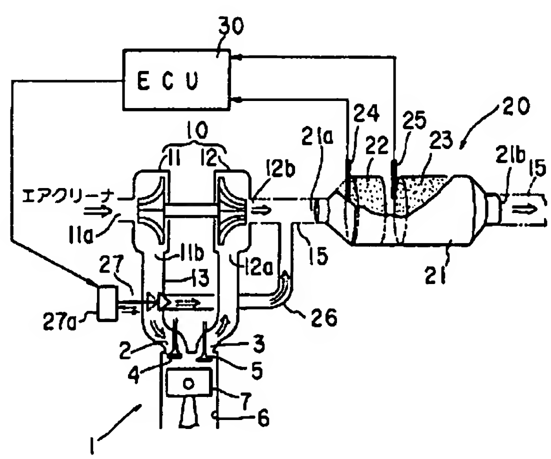
(71)出願人　000006286
三菱自動車工業株式会社
東京都港区芝五丁目33番８号
(72)発明者　海川　敏光
東京都港区芝五丁目33番８号　三菱自動車工業株式会社内
(72)発明者　松井　利治
東京都港区芝五丁目33番８号　三菱自動車工業株式会社内
(74)代理人　100058479
弁理士　鈴江　武彦　（外３名）

最終頁に続く

(54)【発明の名称】　排ガス浄化装置

(57)【要約】
【課題】本発明は、幅広いエンジンの運転領域で、熱劣化や熱による破損を回避しつつ、連続再生による浄化ができる排ガス浄化装置を提供する。
【解決手段】本発明の排ガス浄化装置は、一酸化窒素を二酸化窒素に酸化させる酸化触媒２２と、パティキュレート・マターを捕集するフィルタ２３とを組み合せた連続再生トラップ構造に、酸化触媒２２の上流へ空気を導入する導入構造２６、酸化触媒２２の上流の排ガス温度を検出する温度センサ２４、フィルタ２３へ向かう二酸化窒素の濃度を検出する二酸化窒素センサ２５、さらには温度センサ２４の検出温度が所定値以上で二酸化窒素センサ２５の検出濃度が所定値以下のとき空気が導入されるようにするＥＣＵ３０を組み合せて、排ガスの温度が高くとも、一酸化窒素から二酸化窒素への転化率を高い状態に保ちながら、パティキュレート・マターの十分な酸化除去が進められるようにした。



【特許請求の範囲】

【請求項１】　エンジンの排ガスを排出する排ガス通路に配設され、排ガス中の一酸化窒素を二酸化窒素に酸化させる酸化触媒と、
前記酸化触媒の下流側に配設され、排ガス中のパティキュレート・マターを捕集するフィルタと、
酸化触媒の上流へ空気を導入する空気導入手段と、
前記酸化触媒の上流の排ガス温度を検出する温度センサと、
前記酸化触媒から前記フィルタへ向かう前記二酸化窒素の濃度を検出する二酸化窒素センサと、
前記温度センサの検出温度が所定値以上で、かつ前記二酸化窒素センサの検出濃度が所定値以下のとき、前記空気が導入されるよう前記空気導入手段を制御する制御手段とを具備したことを特徴とする排ガス浄化装置。

【請求項２】　請求項１に記載の排ガス浄化装置において、
前記エンジンは、吸気を過給する過給装置を有した過給式エンジンで構成され、
前記空気導入手段は、前記過給装置の過給した空気の一部を前記酸化触媒の上流へ導入する空気路と、同空気路を開閉する弁装置とを有して構成されることを特徴とする排ガス浄化装置。

【発明の詳細な説明】

【０００１】

【発明の属する技術分野】本発明は、エンジンから排出される排ガス中に含まれるパティキュレート・マターを除去する排ガス浄化装置に関する。

【０００２】

【従来の技術】自動車に搭載されるディーゼルエンジンから排出される排ガス中には、パティキュレート・マター（粒子状物質：以下、ＰＭという）が含まれている。ＰＭは、すすと未燃焼炭化化合物といった可燃性の物質である。

【０００３】そこで、自動車では、ＰＭを酸化処理する排ガス浄化装置を用いて、エンジンから排出される排ガス中のパティキュレート・マターを取り除く研究が進められている。

【０００４】多くは、排ガス浄化装置として、特開昭６１－９３２１９号公報に見られるように、エンジンの排ガスが排出される排ガス通路に、触媒が付いたディーゼル・パティキュレート・オキシダオザ（以下、ＤＰＯという）を配設する構造が提案されている。同装置は、自動車の走行中、ＤＰＯにより、エンジンから排出されるＰＭを捕集する。そして、ＰＭの燃焼に必要な十分な排ガス温度が確保される高負荷時などにおいて過給空気の一部をＤＰＯへ供給し、吸入空気の酸素と排ガスの熱を利用して、捕集したＰＭを燃焼させて、ＤＰＯを再生させるものである。

【０００５】ところで、エンジンから排出される排ガスの温度は、自動車の運転状況により、低温から高温までの幅広い領域で変わるので、排ガス浄化装置は、できるだけ低温の領域からＰＭの酸化除去が行えることが求められる。

【０００６】ところが、上記排ガス浄化装置は、ＤＰＯに付いている触媒により、比較的低温の領域でＰＭの酸化除去が可能であるが、それでもＰＭの酸化温度が４５０℃以上でないと十分なフィルタの再生が得られず、思うような低温域でのＰＭ燃焼が期待できない（試験による）。

【０００７】そこで、酸素（O_2）によりＰＭを酸化するのではなく、二酸化窒素（NO_2）によりＰＭを酸化除去するようにした排ガス浄化装置が提案されている。

【０００８】これは、特開平１－３１８７１５号公報に示されるように、前段に排ガス中の一酸化窒素（以下、ＮＯという）を二酸化窒素（以下、NO_2という）に酸化させる酸化触媒を配置し、後段にＰＭを捕集するＤＰＦを配置した２段式の排ガス浄化装置である。同装置は、前段の酸化触媒により、排気ガス中のＮＯをNO_2まで酸化反応させ（$NO+1/2O_2 \rightarrow NO_2$）、この$NO_2$を利用して、後段のＤＰＦで捕集されたＰＭを燃焼反応（酸化反応：$C+2NO_2 \rightarrow CO_2+2NO$）させて、ＰＭを酸化除去するものである。

【０００９】同技術だと、上記酸化反応により、２５０～３００℃程度の低温域から、連続的にＰＭの酸化除去が可能となる（連続再生）。

【００１０】

【発明が解決しようとする課題】ところが、ＮＯをNO_2に酸化させる酸化触媒は、触媒の特性上、現在、３００℃以上の温度領域になると、ＮＯをNO_2にする能力が低下する現象が表れる。しかも、それ以上の温度域は、酸化触媒での酸化反応により得たNO_2が分解反応（$2NO_2 \rightarrow 2NO+O_2$）を起し、ＮＯに戻ってしまう。

【００１１】これでは、高温領域になると、一部のNO_2が分解してＮＯに戻り、ＰＭの酸化除去に必要なNO_2が不足する（$NO \rightarrow NO_2$の転化率が低下）。

【００１２】つまり、連続再生式の排ガス浄化装置には、ＤＰＦの連続再生が可能な温度領域は狭いという問題がある。

【００１３】このため、同排ガス浄化装置のＰＭ浄化率は、限られた連続再生可能な温度領域の中では良い値を示すがそれ以外の温度領域では低く、自動車に見られるような運転状態に応じて排ガスの温度が低温から高温まで幅広く変化する温度領域では、ＤＰＦの再生は非常に難しい。

【００１４】しかも、酸化触媒は５００℃以上の温度領域だと触媒の熱劣化が始まり、ＤＰＦは１０００℃以上の高温になると破損するおそれがあるので、単純にNO_2を添加するだけでは十分でなく、簡単には連続再生式の排ガス浄化装置を自動車用エンジンの排ガス浄化には

適用できなかった。
【0015】本発明は上記事情に着目してなされたもので、その目的とするところは、低温から高温までの幅広い排ガス温度域で、熱劣化や熱による破損を回避しつつ、連続再生による十分な浄化ができる排ガス浄化装置を提供することにある。
【0016】
【課題を解決するための手段】上記目的を達成するために請求項1に記載の排ガス浄化装置は、一酸化窒素（NO）を二酸化窒素（NO_2）に酸化させる酸化触媒と、排ガス中のパティキュレート・マター（PM）を捕集するフィルタとを組み合せた連続再生トラップ構造に、酸化触媒の上流へ空気を導入する空気導入手段、酸化触媒の上流の排ガス温度を検出する温度センサ、酸化触媒からフィルタへ向かう二酸化窒素の濃度を検出する二酸化窒素センサ、さらには温度センサの検出温度が所定値以上で二酸化窒素センサの検出濃度が所定値以下のとき空気が導入されるよう空気導入手段を制御する制御手段を組み合せて、酸化触媒の酸化反応に最適な触媒活性温度を超える排ガス温度のとき、空気を酸化触媒の上流へ導入するようにした。
【0017】この構成だと、連続再生式の排ガス浄化装置が、二酸化窒素の不足からフィルタの連続再生が望めない状態になると、導入される空気により、酸化触媒が冷却される。すると、酸化触媒は、排ガス中の一酸化窒素を二酸化窒素に酸化反応させるのに最適な触媒活性温度（例えば300℃前後）に保たれる。しかも、酸化触媒は、空気中に含まれる酸素の添加により、酸化反応が促進されるだけでなく、二酸化窒素の分解反応が抑えられる。こうした触媒温度がほぼ一定に保たれる状態での酸化反応により、排ガス温度が高くとも、酸化触媒は高い転化率で一酸化窒素から二酸化窒素への酸化反応が行なわれる。
【0018】後段のフィルタへ向かう二酸化窒素は、空気の導入がもたらす冷却や同空気の酸素により、分解が抑制される。これにより、フィルタのパティキュレート・マターを燃焼（酸化）させるのに最適な二酸化窒素の濃度が確保されるので、フィルタに付いているパティキュレート・マターが十分に酸化除去される。
【0019】かくして、空気の導入により、排ガスの温度が高くとも、一酸化窒素から二酸化窒素への転化率を高い状態に保ちながら、パティキュレート・マターの十分な酸化除去が進められるので、浄化性能を向上できる。
【0020】そのうえ、酸化触媒、フィルターは、導入空気による冷却により、熱劣化や熱による破損が回避されるので、耐久性の向上が図れる。
【0021】請求項2に記載の排ガス浄化装置は、上記目的に加え、さらにエンジンに付いている補機を活用して、コスト的な負担を抑えつつ空気の導入が行えるよう、過給装置を有した過給式エンジンを採用することを前提とした上で、空気導入手段として過給装置の過給した空気の一部を酸化触媒の上流へ導入する空気路と同空気路を開閉する弁装置との組み合わせを採用するようにした。
【0022】
【発明の実施の形態】以下、本発明を図1ないし図3に示す一実施形態にもとづいて説明する。
【0023】図1中1は、自動車に搭載される走行用ディーゼルエンジンを示す。ディーゼルエンジン1は、吸・排気ポート2，3、同吸・排気ポート2，3を開閉する吸・排気弁4，5、燃料噴射ノズル（図示しない）を有するシリンダ6内に、ピストン7を往復動可能に収めて構成される。そして、同エンジン1は、ピストン7の往復動にしたがい、所定のタイミングで吸・排気弁4，5が開閉動、さらには所定のタイミングで燃料噴射ノズルから燃料が燃焼室へ噴射されることにより、シリンダ6内で吸入行程、圧縮行程、燃焼行程、排気行程が周期的に行なわれ、ピストン2とつながるクランクシャフト（図示しない）から動力が出力されるようにしてある。
【0024】このディーゼルエンジン1の吸気ポート2は、過給機、例えばターボ過給機10を構成しているコンプレッサ11の出口11bに接続されている。また排気ポート3は、コンプレッサ11と同軸に連結されているターボ過給機10のタービン12の入口12aに接続されている。このターボ過給機10が付くことにより、吸入空気が、排ガスの排気エネルギーで、ディーゼルエンジン1の燃焼室へ過給されるようにしている。つまり、過給式ディーゼルエンジンとしている。なお、コンプレッサ11の入口11aは、図示しないがエアクリーナーに接続される。
【0025】またタービン12の出口12bには、排気管15（排ガス通路）が接続されていて、同排気管15からディーゼルエンジン1の排ガスが外部（大気）へ排出されるようにしてある。
【0026】この排気管15の途中には、排気ガス中のパティキュレート・マターを酸化除去する排ガス浄化装置20が介装されている。
【0027】同装置は、例えば排気管15の上流側につながる入口21aを一端部に有し、排気管15の下流側につながる出口21bを他端部に有した1つの共通な細長のケース21を有している。このケース21内の上流側（前段）には、一酸化窒素（以下、NOという）を二酸化窒素（以下、NO_2という）に酸化させる酸化触媒22を収めてある。またケース21内の下流側（後段）には、パティキュレート・マター（以下、PMという）を捕集するディーゼルパテキュレートフィルタ23（以下、DPF23という：本願のフィルタに相当）が収めてある。これら直列に配設された酸化触媒22、DPF23により、2段式の連続再生式トラップを構成してい

る。そして、この連続再生式トラップにより、前段の酸化触媒２２で排気ガス中のＮＯをNO_2まで酸化反応させ（$NO+1/2O_2 \rightarrow NO_2$）、この$NO_2$を利用して、後段のＤＰＦで、捕集されたＰＭを燃焼反応（酸化反応：$C+2NO_2 \rightarrow CO_2+2NO$）させて、排ガス中のＰＭの酸化除去を可能としている。

【００２８】この排ガス浄化装置２０のうち、ケース２１の上流側には、酸化触媒２２の上流側の排ガス温度を検出する温度センサ２４が組み付けてある。さらにケース２１の中間部分には、酸化触媒２２からＤＰＦ２３へ向かうNO_2の濃度を検出する二酸化窒素センサ２５（以下、NO_2センサ２５という）が組み付けてある。

【００２９】また酸化触媒２２の上流側の地点、例えば入口２１ａの直前の排気管１５部分には、空気導入管２６（空気路に相当）の一端部が接続されている。この空気導入管２６の他端部は、ディーゼルエンジン１の吸気ポート２とコンプレッサ１１の出口１１ｂとをつなぐ吸気路１３の一部に接続されていて、これによりターボ過給機１０で過給した空気の一部が酸化触媒２２の上流側へ導入できるようにしている。この空気導入管２６の経路には、空気の導入を制御するアクチュエータ、例えばソレノイド２７ａで開閉駆動される弁装置２７が組み付けられていて、同弁装置２７で空気導入管２６が開閉できるようにしている（本実施形態では常閉形の弁装置２５）。

【００３０】そして、温度センサ２４、NO_2センサ２５、弁装置２７のソレノイド２７ａは、例えばマイクロコンピュータで構成されたＥＣＵ３０（制御手段に相当）に接続されている。このＥＣＵ３０には、自動車の走行中、酸化触媒２２へ向かう排ガスの温度が酸化触媒２２の最適活性化温度（所定値：例えば３００℃）以上、すなわち最適活性化温度が保てなくなるときで、かつＤＰＦ２３へ向かうNO_2濃度が、予めディーゼルエンジン１の運転状態から設定したＰＭの酸化除去に必要な濃度［例えばＰＭモル濃度の２倍（所定値：酸化反応式による）］以下、すなわちＰＭの酸化除去に必要なNO_2が不足するとき、常閉の弁装置２７を開作動させる機能が設定されている。つまり、当該エンジン運転状態のときにだけ、多くの酸素を含む低温度の吸入空気が、酸化触媒２２の上流側から導入されるようにしてある。

【００３１】この吸入空気の導入により、連続再生式トラップにおいて、排ガス温度に関わらず、連続的な再生処理で、十分なＰＭの酸化処理が果たせるようにしてある。図２のフローチャートは、この連続再生式トラップの制御が示されている。

【００３２】同フローチャートにもとづき連続再生式トラップの作用について説明すれば、今、ディーゼルエンジン１が、自動車の走行に伴い、運転されているとする。

【００３３】このとき、シリンダ６から排出された排ガスは、ターボ過給機１０のタービン１２、排気管１５、排ガス浄化装置２０（連続再生式トラップ）を通じて、外部（大気）へ排気される。なお、ターボ過給機１０は、タービン１２によるコンプレッサ１１の駆動により、吸入空気を過給している。

【００３４】そして、排ガスが排ガス浄化装置２０を通過する際、排ガス中のＰＭが後段のＤＰＦ２３で捕集され、同ＰＭが前段の酸化触媒２３で生成されるNO_2で、連続的に燃焼（酸化除去）される。

【００３５】すなわち、今、排ガス温度Ｔ（温度センサ２４で検出される温度）が、酸化触媒２２の最適な活性化温度域（例えば３００℃を下回る温度域）に保たれ（ステップＳ１）、ＤＰＦ２３の入口に流入するNO_2濃度Ｒ（NO_2センサ２５で検出される濃度）が、予めエンジン運転状態に応じて設定された設定NO_2濃度（［NO_2］：エンジン運転状態から求めたＰＭモル濃度の２倍）を超える濃度に保たれて（ステップＳ２）いるとする。

【００３６】すると、ＥＣＵ３０は、今のエンジン運転状態が、ＤＰＦ２３の連続再生温度領域を保つ状態にあると判定して、弁装置２７を「閉」にする（ステップＳ３）。

【００３７】このときは、排ガスの温度は低いので（３００℃未満）、排ガス浄化装置２０は、前段の酸化触媒２２において、排気ガス中のＮＯをNO_2まで酸化させる反応（$NO+1/2O_2 \rightarrow NO_2$）が十分に行なわれる。そして、この$NO_2$により、後段のＤＰＦ２３において、捕集されたＰＭを燃焼反応（酸化反応：$C+2NO_2 \rightarrow CO_2+2NO$）させるという、連続的なＰＭの酸化除去が行なわれる。

【００３８】一方、自動車の運転状態により、排ガス温度Ｔが設定排ガス温度（３００℃）以上に上昇し、酸化触媒２２におけるＮＯをNO_2まで酸化させる反応が低下し（ステップＳ１）、さらにＰＭの酸化除去に必要なNO_2濃度が確保されなく（ステップＳ２）なったとする。

【００３９】このときには、ＥＣＵ３０は、二酸化窒素の不足からＤＰＦ２３の連続再生が望めない状態になったと判定して、弁装置１を「開」にする（ステップＳ４）。

【００４０】すると、ターボ過給機１０で過給されたの過給空気の一部（低温でかつ多くの酸素を含む空気）が、空気導入管２６を通じて、酸化触媒２２の上流へ導入される。

【００４１】これにより、酸化触媒２２は、導入空気により冷却され、ＮＯをNO_2に酸化反応させるのに最適な触媒活性化温度（例えば３００℃前後）に保たれる。と同時に、空気中に含まれる酸素の添加により、上記酸化反応が促進される。むろん、NO_2からＮＯへの分解反応は抑えられる。

【0042】このような触媒温度がほぼ一定に維持されることにより、排ガス温度Tが高くとも、酸化触媒22は、高い転化率で、NOからNO_2への酸化反応が行なわれる。

【0043】そして、このNO_2が、後段のDPF23へ導かれる。このNO_2は、導入空気による冷却や空気中の酸素による安定化により、分解が抑制される。これにより、NO_2濃度の低下が抑制され、PMを燃焼（酸化）させるのに最適なNO_2濃度は確保される。このNO_2により、DPF23に付いているPMが十分に酸化除去される。

【0044】かくして、空気の導入により、排ガスの温度が高くとも、NOからNO_2への転化率を高い状態に保ちながら、DPF23で十分なPMの酸化除去が進められる（連続再生の維持）。

【0045】このことにより、DPF23の連続再生温度領域は、限られた運転状態でなく、高温の排ガスを排出する運転状態においても、PMを効率良く浄化することができる。

【0046】特に、導入空気がもたらす冷却作用と、導入空気の酸素の添加作用とがもたらす共存効果により、単に酸化触媒22とDPF23との2つの反応系を組み合せて得られるPM浄化率よりも、高いPM浄化率が得ることができる（浄化能力の向上）。すなわち、図3は、リグ試験による同効果を線図化したもので、同図（a）はPM（C）とNO_2との反応で行なわれるPMの浄化率を示し、（b）はPM（C）とO_2との反応でPM行なわれるPMの浄化率を示し、（c）は両反応系に空気の導入を組み合せたときのPMの浄化率を示している。（c）と他の（a），（b）を対比することによって、O_2が酸化触媒22とDPF23の双方でもたらす冷却・酸素添加の有効性から、単に（a）と（b）と加算した以上のPM浄化率（PM浄化能力）が得られることがわかり、連続再生式トラップの浄化能力が促進されたことが確認された（リグ試験による）。但し、PM浄化率は、「加熱前後PM堆積量の差A／加熱前のPM堆積量B」で表されるパラメータである。

【0047】そのうえ、酸化触媒22、DPF23は、導入空気による冷却により、熱劣化や熱による破損が回避されるので、耐久性の点にも優れる。

【0048】また導入空気は、ディーゼルエンジン1に付いている補機であるターボ過給機10を、そのまま、低温かつ多量の酸素を含む空気を供給する供給源として活用して、酸化触媒22の上流へ導入するようにしたので、別途、空気供給源は必要でなく、コスト的な負担は軽くてすむ。

【0049】なお、本発明は上述した実施形態に限定されることなく、本発明の主旨を逸脱しない範囲内で種々変更して実施しても構わない。例えば上述した一実施形態では、ターボ過給機の過給空気の一部を酸化触媒の上流へ導入させるようにしたが、それ以外の過給機を用いて、酸化触媒の上流へ空気を導入させるようにしてもよい。

【0050】

【発明の効果】以上説明したように請求項1に記載の発明に記載の発明によれば、空気の導入により、排ガスの温度が高くとも、一酸化窒素から二酸化窒素への転化率を高い状態に保ちながら、パティキュレート・マター（PM）の十分な酸化除去が進められる。

【0051】したがって、従来、所定運転領域（排ガス温度が300℃前後の運転領域）でしかパティキュレート・マターを効率良く燃焼除去できなかったのに対して、本発明の場合、排ガス温度が300℃よりも高い運転状態の時でも酸化触媒の温度を最適温度に維持できるので、幅広い運転領域でフィルタの連続再生ができる。しかも、導入空気が、酸化触媒とフィルタの双方でもたらす冷却・酸素添加により、連続再生式トラップで構成される排ガス浄化装置は、今まで以上の浄化能力の向上を図ることができる。そのうえ、酸化触媒、フィルターは、導入空気による冷却により、熱劣化や熱による破損が回避されるので、耐久性の点にも優れる。

【0052】請求項2に記載の発明によれば、上記効果に加え、エンジンに付いている補機である過給機の過給空気の一部を酸化触媒の上流へ導入させるようにしたので、外部から空気を導入するに際し、別途、空気供給源を設置せずにすみ、コスト的な負担を抑えつつ空気の導入ができるといった効果を奏する。

【図面の簡単な説明】

【図1】本発明の一実施形態に係る排ガス浄化装置を、同装置を組み付けたエンジンと共に示す図。

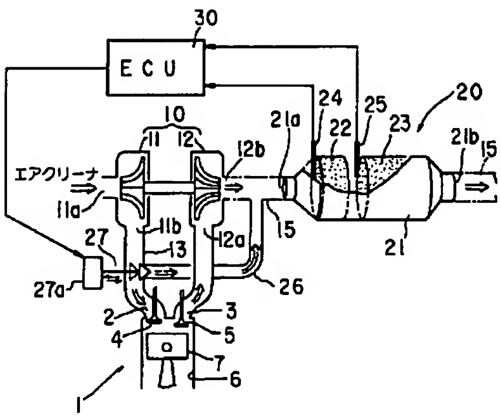
【図2】同排ガス浄化装置の連続再生能力を、排ガスの温度に関わらずに発揮させる制御を説明するためのフローチャート。

【図3】同連続再生能力が、リグ試験で導入空気により、促進されることを説明するための線図。

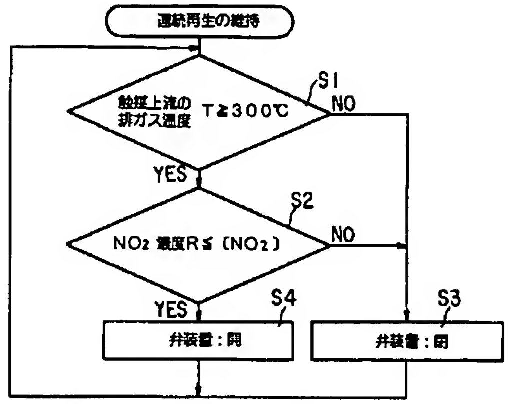
【符号の説明】

1…ディーゼルエンジン（エンジン）
10…ターボ過給機（過給機）
15…排気管（排ガス通路）
21…ケース
22…酸化触媒
23…パティキュレート・フィルタ（フィルタ）
24…温度センサ
25…二酸化窒素センサ
26，27…空気導入管，弁装置（空気導入手段）
30…ECU（制御手段）。

【図1】

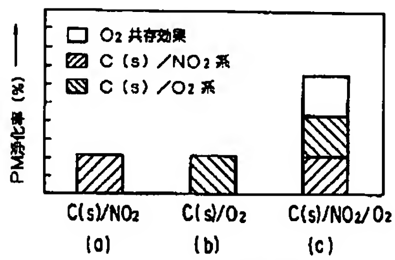


【図2】



〔NO_2〕：NO_2モル濃度＝PMモル濃度×2

【図3】



PM浄化率＝A／B：
A：加熱前後PM推積量の差；
B：加熱前PM推積量.

フロントページの続き

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